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Extrinsic Substrate Orientation Dependence of Ferromagnetism in (Ga,Mn)As Digital Ferromagnetic Heterostructures

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14. ABSTRACT

We describe the structural and magnetic properties of digital ferromagnetic heterostructures of (Ga,Mn)As grown on (001), (311), (201) and (110) GaAs surfaces. Our measurements show a systematic variation of the Curie temperature with epitaxial orientation for samples with a nominally identical structure. Control measurements of randomly alloyed (Ga,Mn)As grown on these substrates show identical trends in Curie temperature, suggesting that the substrate orientation plays a strong role in the formation of hole-compensating defects in this ferromagnetic semiconductor.

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"Controlling Spins in Semiconductor Devices," N. Samarth, 14th International Workshop on Physics of Semiconductor Devices: Plenary Talk, 12/18/2007 Indian Institute of Technology, Mumbai India.

"Substrate Orientation Dependence of Ferromagnetism in Ferromagnetic Semiconductor Superlattices," N. Samarth, DARPA Workshop on Predicting Real Optimized Materials, Tucson AZ, November 2007.

"Spin Control in Magnetic Semiconductor Heterostructures," N. Samarth, WUN International Workshop on Spintronics, Youk, United Kingdom, August 2007.

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S. May, A. Bhattacharya (submitted to Applied Physics Letters)

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Mark Wilson	1.00
Ben Li Sheu	0.25
FTE Equivalent:	**1.25**
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Gang Xiang	1.00
FTE Equivalent:	**1.00**
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Names of Faculty Supported

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Extrinsic Substrate Orientation Dependence of Ferromagnetism in (Ga,Mn)As Digital Ferromagnetic Heterostructures.

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Abstract

We describe the structural and magnetic properties of digital ferromagnetic heterostructures of (Ga,Mn)As grown on (001), (311), (201) and (110) GaAs surfaces. Our measurements show a systematic variation of the Curie temperature with epitaxial orientation for samples with a nominally identical structure. Control measurements of randomly alloyed (Ga,Mn)As grown on these substrates show identical trends in Curie temperature, suggesting that the substrate orientation plays a strong role in the formation of hole-compensating defects in this ferromagnetic semiconductor.

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The "canonical" ferromagnetic semiconductor $\mathrm{Ga_{1-x}Mn_xAs}$ has been the focal point of research in semiconductor spintronics for reasons of fundamental interest and for proof-of-concept device applications.[1] Thus far, the Curie temperature (T_{C}) in $\mathrm{Ga_{1-x}Mn_xAs}$ has been limited to below ~ 190 K, presumably constrained by hole-compensating defects and limits on the incorporation of substitutional Mn. Within the mean field Zener model, the path to higher values of T_{C} requires increasing the substitutional Mn concentration, while minimizing the defect concentration.[2] Alternative theoretical viewpoints have proposed a different route to enhancing T_{C} by controlling the geometrical arrangement of Mn atoms within the $\mathrm{Ga_{1-x}Mn_xAs}$ lattice. In particular, a first-principles combinatorial calculation[3] has predicted large and systematic variations in T_{C} for $\mathrm{(GaAs)}_m\mathrm{(MnAs)}_1$ short period superlattices – or "digital ferromagnetic heterostructures" (DFHs)[4] – grown along different epitaxy directions. In particular, this calculation predicts that DFHs grown on (201) substrates, a previously unexplored orientation, would lead to higher T_{C} than both random alloy samples and DFHs grown on any other substrate orientation. The predicted dependence of T_{C} on substrate orientation has its origins in the highly anisotropic nature of the Mn-Mn exchange interaction, as revealed by multiband tight-binding[5] and first principles calculations,[6] as well as by scanning tunneling spectroscopy.[7] The expected variation of T_{C} with substrate orientation provides an opportunity for unambiguous experimental tests of first principles calculations and is a strong motivation for the systematic experimental exploration of the growth of DFHs on different substrate orientations.

In this Letter, we present a comprehensive study of the structural and magnetic properties of $\mathrm{Ga_{1-x}Mn_xAs}$ DFH and random alloy samples grown on four different substrate orientations: (001), (311), (201) and (110). We find a systematic variation of T_{C} with substrate orientation, but the experimental results are superficially inconsistent with the theoretical predictions. By carefully examining $\mathrm{Ga_{1-x}Mn_xAs}$ random alloys grown on the same substrate orientations, we show that this discrepancy most likely has *extrinsic* origins and may be explained by the variation in As antisite defect density with substrate orientation. Our study also highlights the challenging experimental hurdles that need to be overcome in order to provide meaningful comparisons with theory.

The samples are grown by molecular beam epitaxy on semi-insulating GaAs substrates with different orientations. Substrates are mounted on indium-bonded molybdenum blocks, and the substrate temperature is carefully monitored using band-edge thermometry. We use high purity elemental sources of Ga (5N), As (5N) and Mn (4N), evaporated from standard effusion cells. The growth is monitored using reflection high energy electron diffraction (RHEED) at 12 keV. RHEED oscillations are used to calibrate the growth rate of GaAs and MnAs on (001) GaAs. Since we have not succeeded in observing RHEED oscillations on other substrate orientations, we scale this growth rate by the respective surface densities for the other 3 substrate orientations, assuming a constant sticking coefficient. We first deposit an undoped, 180 nm thick GaAs buffer layer under standard conditions (substrate temperature of 600°C). The temperature is then reduced to 290°C for the growth of the (Ga,Mn)As layer. DFH samples are grown by alternating GaAs and MnAs growth. Random alloy samples are grown by co-depositing all three elements simultaneously.

Theoretical predictions have primarily focused on $(\mathrm{MnAs})_1/(\mathrm{GaAs})_m$ DFHs that contain a full monolayer (ML) of MnAs in each unit. However, as reported in the first study of DFH growth on (001) GaAs,[4] we find that it is difficult to maintain good crystallinity with more than ~ 0.5 monolayer coverage of MnAs. Thus, we restrict our DFH geometry to contain 30 repeats of units that contain a 0.5 ML coverage of MnAs, and a GaAs spacer whose thickness varies from 4.5 to 9.5 monolayers. In the absence of diffusion, such samples would ideally correspond to superlattices in which each unit consists of $(\mathrm{Ga}_{0.5}\mathrm{Mn}_{0.5}\mathrm{As})_1/(\mathrm{GaAs})_m$, where $4 \leq m \leq 9$. High resolution cross-sectional transmission electron microscopy (TEM) reveals significant interdiffusion: for instance, for growth on (001) substrates, we can clearly discern distinct layers for DFH samples with $m \geq 7$ but not for samples with shorter periods (Fig. 1(a)). We estimate a Gaussian diffusion profile of the Mn with a diffusion length of roughly 3 nm, similar to previous studies.[4] The inhomogeneous distribution of Mn atoms nothwithstanding, secondary ion mass spectroscopy (SIMS) measurements of nominally identical superlattices grown on different orientations show an identical average Mn concentration. Additional structural characterization is carried out using x-ray reflectometry (Fig.1(b)). These measurements reveal a clear signature of superlattice formation in (001)-oriented samples. In addition, we observe Pendellösung thickness fringes due to the total thickness of the GaAs buffer layer and the superlattice in (001)- and (311)-oriented samples. The (201) and (110)-oriented samples were too rough to see these effects.

We carry out temperature-dependent magnetization measurements using a Quantum Design dc superconducting quantum interference device (SQUID). The samples are cooled under a 10 kOe field and measured during warming with an applied field of 50 Oe for the

DFHs and 200 Oe for the random alloys. The measuring field is applied in plane, near the anticipated easy axis for each sample. We note however that it is difficult to do this for some of the non-standard substrate orientations such as the (201) substrates. We have verified that the Curie temperature is independent of the direction of applied field. In Fig. 2(a), we show the magnetization as a function of temperature for the different DFH samples with a 7.5 ML GaAs spacer. The data indicate a clear substrate orientation dependence on $T_{\rm C}$. This trend is robustly followed by an entire set of samples where we vary the spacer thickness (Fig. 2(b)). For a fixed spacer thickness, the (001) substrate orientation shows the highest $T_{\rm C}$. As expected, for any given substrate orientation, $T_{\rm C}$ decreases with increasing spacer thickness. The substrate orientation dependence of $T_{\rm C}$ is clearly inconsistent with theoretical predictions.

In order to ascertain whether the experimental observations have an intrinsic origin or an extrinsic one, we carry out a set of systematic experiments. First, we explore whether the variations in $T_{\rm C}$ show any correlation with hole concentrations in the different samples. We estimate the carrier concentration by using Hall effect measurements at room temperature; in these relatively low $T_{\rm C}$ samples, contributions from the anomalous Hall effect are small and – in any case – our measurements can reveal *relative* variations in hole density. We carry out a linear fit to the Hall resistance as a function of magnetic field from 5 to 9 T and find a suggestive correlation between $T_{\rm C}$ and hole density (Fig. 2 (c)). These data indicate that extrinsic factors may be at the root of the observed orientation dependence of $T_{\rm C}$.

To further examine the origins of the substrate-orientation dependence of $T_{\rm C}$ in the DFH samples, we explore a series of 30 nm thick random alloy $\rm Ga_{1-x}Mn_xAs$ epilayers on the four substrate orientations. We have grown sets of samples, nominally with $x = 0.05$ and $x = 0.08$. In order to eliminate possible growth condition variations, we mount all four substrates on the same molybdenum block and grow them simultaneously. Figure 3(a) shows that the random alloys exhibit the same dependence of $T_{\rm C}$ on substrate orientation as the DFH samples. These observations are consistent with the results of a recent study comparing growth of $\rm Ga_{1-x}Mn_xAs$ epilayers on (001), (311) and (110) oriented substrates. [8] We caution though that this previous study did not eliminate variations in sample to sample growth or provide a specific reason for the $T_{\rm C}$ dependence on orientation. Figure 3(b) shows that the hole concentration in our random alloy samples is also dependent on substrate orientation, and correlates roughly with the trends in $T_{\rm C}$. Figure 3(c) shows SIMS data for the four random alloy samples, indicating that the Mn concentration is identical among all the samples, thus ruling out variations in Mn incorporation. Our observations suggest that the substrate orientation has a strong effect on the formation of hole-compensating defects.

It is now well-established that two types of hole-compensating defects dominate the magneto-electronic properties of $Ga_{1-x}Mn_xAs$: Mn interstitials and As antisites, both of which act as double donors. [2] The former can be removed to the free surface of the sample by post-growth annealing at relatively low temperatures ($T \lesssim 250°C$.[9] In contrast, there is presently no evidence that As antisites are affected during such low temperature annealing. Figure 3(d) shows T_C of the random alloy samples as a function of annealing. These data indicate that – although annealing does enhance T_C in all the random alloy samples – it does not affect the relative variations in T_C between different orientations. Thus, it is unlikely that the substrate orientation affects the formation of Mn interstitials; instead, we conclude that variations in the formation of As antisites must be responsible for our observed variation of T_C and hole density for samples with different substrate orientations.

In conclusion, our extensive study has clearly established the growth conditions necessary for epitaxial growth of random and digital (Ga,Mn)As alloys on four different substrate orientations: (001), (311), (201) and (110). We have found a systematic substrate orientation dependence of T_C in both random alloy and DFH samples of $Ga_{1-x}Mn_xAs$, with (001)-oriented samples giving the highest values of T_C and (110)-oriented samples giving the lowest T_C. These variations do not agree with theoretical predictions but are not intrinsic: they can be traced to different densities of hole-compensating As antisites. We conclude that meaningful experimental tests of first principles theory remain a daunting challenge for materials growth.

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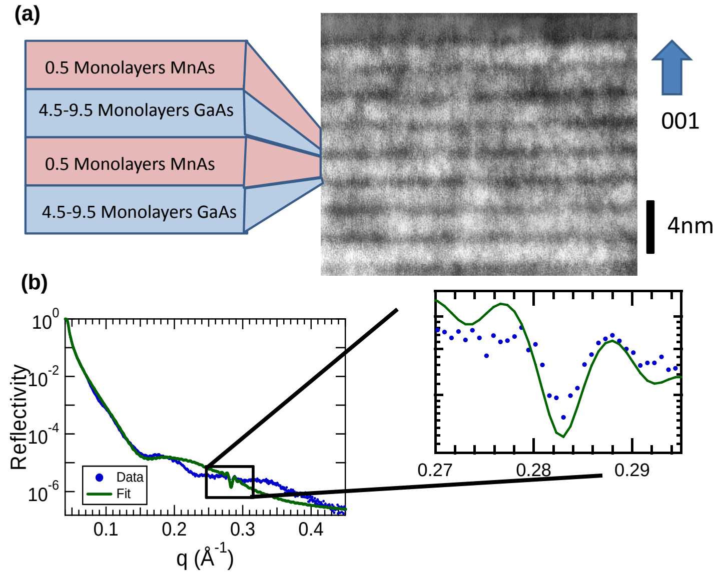

FIG. 1: (a) High-angle annular dark-field TEM image of a (001)-oriented DFH with 0.5 ML MnAs and 7.5 ML GaAs spacer. Structure has 30 periods and the image clearly shows distinct layers. (b) X-ray reflectivity data showing a peak corresponding to the expected superlattice periodicity.

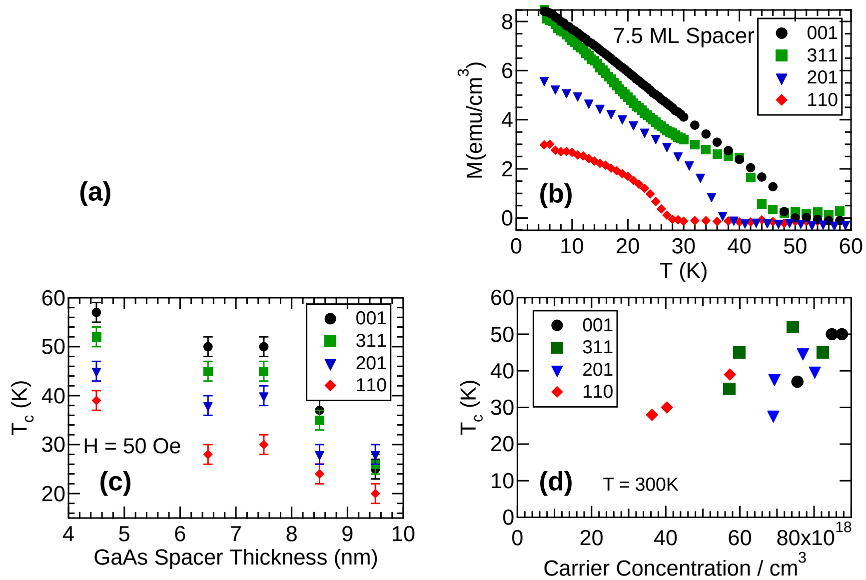

FIG. 2: (a) Magnetization vs. temperature for DFH grown on (201) substrate orientation along different measuring field directions. (b) Magnetization vs. temperature for DFH with a fixed 7.5 ML spacer and different substrate orientations. (c) T_C as a function of spacer thickness for DFH samples with different substrate orientations. (d) Variation of T_C with hole density in DFH samples with varying substrate orientation and spacer thickness.

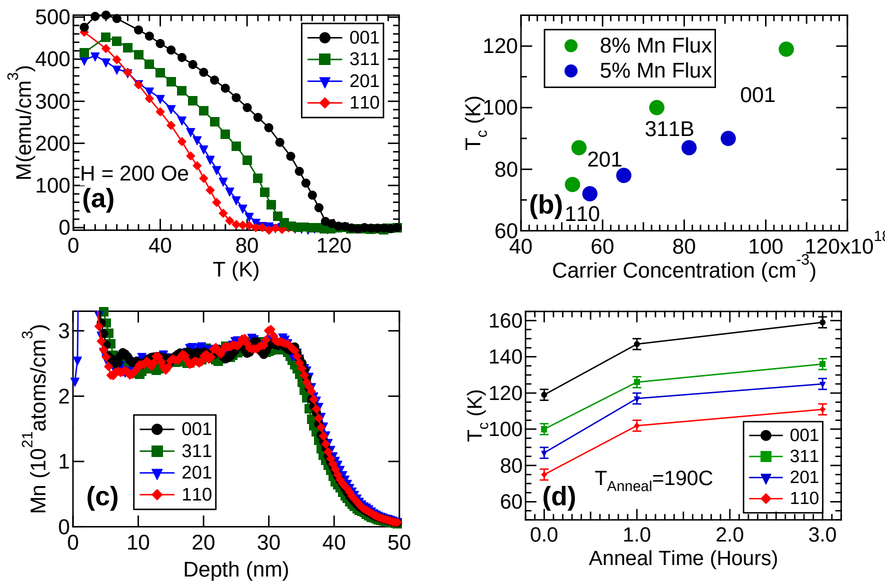

FIG. 3: (a) Magnetization vs. temperature for random alloy samples showing similar trends as DFH samples. (b) Variation of T_C with hole density for random alloy samples of varying substrate orientation and different Mn concentration. (c) SIMS analysis of Mn concentration in random alloy samples with different substrate orientations, showing identical Mn incorporation. The increased Mn concentration near the sample surface may be the result of unintentional annealing. (d) Effect of annealing on T_C, showing that difference in Mn interstitial densities between orientations is unlikely.